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Approaching the *s*-wave model ground state energy of He-like atomic ions: results from a model Hamiltonian

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Abstract

Amovilli, Howard and March model Hamiltonian is here extended to an arbitrary interparticle interaction strength. The model remains analytically solvable and the ground state wavefunction with a given, variationally determined, choice of parameters provides an approximate two-electron correlated *s*-wave function. Results are given for the series of nuclear charges between $Z = 1$ and 10. More than 60 percent of *s*-wave correlation energy is recovered.

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1 Introduction

The so-called s-wave model of helium was first proposed by Temkin [1]. The model, which has proven particularly useful for attacking scattering problems (see, e.g. the book of McGuire [2]), is based on the spherical average of the electron interaction potential e^2/r_{12}. Due to this average, the Legendre expansion of the potential is then truncated to the first term. However, the ground-state wave function of the relevant simplified Hamiltonian has not yet proved analytically tractable.

Amovilli, Howard and March (AHM) [3] proposed a new model Hamiltonian by adding to the Temkin s-wave Hamiltonian an electron-electron contact type interaction of the form $\delta(r_1 - r_2)$. The resulting problem is now analytically solvable. Howard and March [4] and Amovilli and March [5] discussed in detail, respectively, the properties of the corresponding one-particle density and density matrix. Nevertheless, the ground-state wave function of the AHM model constitutes a rather poor approximation to the exact solution of the real two-electron system [6, 7].

In this work, we show that, by extending the AHM model to an effective interparticle interaction, one can get a very simple and compact wave function variationally better than the Hartree-Fock one and that recovers a substantial fraction of the s-wave correlation energy.

2 Theory and illustrative examples

The AHM model atom Schrödinger equation has ground-state analytical solution that we can generalize to any interparticle interaction strength as follows, in atomic units,

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{\xi}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{\xi}{r_2} + \frac{\lambda}{r_>} + \lambda\delta(r_1 - r_2)\right] \exp\left[-\xi r_< - (\xi - \lambda) r_>\right] = \left[-\frac{\xi^2}{2} - \frac{(\xi - \lambda)^2}{2}\right] \exp\left[-\xi r_< - (\xi - \lambda) r_>\right] \quad (1)$$

where $r_> = [r_1 + r_2 + |r_1 - r_2|]/2$ and $r_< = [r_1 + r_2 - |r_1 - r_2|]/2$. Here,

$$\Psi[\xi, \lambda](r_1, r_2) \propto \exp\left[-\xi r_< - (\xi - \lambda) r_>\right] \tag{2}$$

is the 'model' ground-state wave function and

$$E = -\frac{\xi^2}{2} - \frac{(\xi - \lambda)^2}{2} \tag{3}$$

is the corresponding ground-state energy. If we take $\xi = Z$ and $\lambda = 1$ of a two electron atomic ion, $\Psi[Z, 1]$ is a very poor approximate solution for the real system with a mean value of the real Hamiltonian much above the Hartree-Fock energy [6, 7]. So, here we attempt the search of optimal ξ and λ for an external confinement due to a nucleus with charge Z by minimizing the functional

$$H = \frac{< \Psi[\xi, \lambda]| - \frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}|\Psi[\xi, \lambda] >}{< \Psi[\xi, \lambda]|\Psi[\xi, \lambda] >} \, . \tag{4}$$

$H(\xi, \lambda)$ of the above Eq.(4) represents the approximate real system energy and has the following expression

$$H(\xi, \lambda) = \frac{\xi^2}{2} + \frac{(\xi - \lambda)^2}{2} - Z(2\xi - \lambda) + \xi - \lambda - \lambda f(\xi/\lambda) \tag{5}$$

where

$$f(z) = \frac{12(z-1)^2(2z^2 - 3z + 1)}{(2z-1)(32z^2 - 50z + 20)} \tag{6}$$

comes from Amovilli et al [3] source paper. The functional H is rather simple and it has an absolute minimum for Z greater than a critical value smaller than 1. We remind that in the present modified model we must have $\xi > \lambda$ for a confinement of the two electrons. When $\xi < \lambda$ the wave function in Eq. (2) diverges for $r_> \to \infty$.

We have studied $H(\xi, \lambda)$ in the range of nuclear charges between 1 and 10. Results are collected in Table 1. In the same Table we report also, for comparison purposes, Hartree-Fock and s-wave energies derived from a configuration interaction with single and double excitations (CISD) calculation

in which we limited the atomic basis set to a large number of elementary spherical Gaussian s-type functions. We performed this computation by using the Gaussian 09 package [8]. Finally, the fully correlated best literature data are displayed in the last column of Table 1.

All optimal energies, namely the minima of $H(\xi, \lambda)$ at various Z, lie below the Hartree-Fock energy although remain above the numerical ground-state energy of the $s-$wave model. Nevertheless, the amount of correlation energy recovered is more than 20 percent of the total and about 60 percent of the s-wave one.

We have also searched the critical value of the nuclear charge at which $H(\xi_{opt}, \lambda_{opt})$ is the same of the hydrogenic like ion, namely $-Z_{cr}^2/2$. The two energies are the same within the numerical error at the critical nuclear charge of 0.9798 a.u. With this external charge, ξ_{opt} and λ_{opt} are, respectively, 0.9015 and 0.5178. In Figure 1, we show the curves for $H(\xi_{opt}, \lambda_{opt})$, s-wave energy and fully correlated energy as a function of the nuclear charge for He-like ions in the range of $Z < 1$. Fully correlated data are taken from our recent work [11]. The three curves touch the function corresponding to the hydrogenic ion at different Z consistently with the amount of correlation energy recovered, the energy of the hydrogenic ion being exact. In a recent paper, Glasser et al [12] pointed out that the AHM model has exactly one as nuclear critical charge but we remark that this is valid only when $\xi = Z$ and $\lambda = 1$.

Finally, there is one more interesting aspect of this study related to the density. Here, we have a model system and a real system that share, essentially, the same density. By way of example, in Figure 2 we show the comparison between the accurate diffusion Monte Carlo (DMC) He radial density[13] and the radial density calculated from $\Psi[\xi_{opt}, \lambda_{opt}]$ with optimal ξ and λ obtained for $Z = 2$. The agreement between the two functions is rather good although we have to remark that Kato cusp condition, for the model case, is not satisfied, ξ_{opt} being different from 2. Nevertheless, it seems that there is a nearly adiabatic connection in going from the Kohn-Sham equation for the density amplitude to the fully interacting system, represented by

the DMC calculation, and passing through the present modified model, with optimal parameters ξ and λ, and the Temkin model. The latter two models are, in fact, representatives of partially interacting electron systems.

3 Conclusions

In this work, we have shown that, modifying the AHM model Hamiltonian [3] by changing the interparticle interaction strength, it is possible to go beyond the Hartree-Fock description of the electron distribution of a He-like ion. The AHM model is obtained from the s-wave model of Temkin [1] by adding a contact like interaction between the two electrons. As shown in Eq. (1), the modified model atom has an analytical ground state solution. This wave function depends on the strength of interparticle interactions, namely ξ for electron-nucleus and λ for electron-electron, and for an appropriate choice of such parameters leads to an approximate s-wave function which recovers about 60 percent of s-wave correlation energy. The optimal parameters give the minimal expectation energy of the real system. Results are shown for He-like ions with nuclear charge up to 10 in atomic units. The critical nuclear charge, at which the ionization potential goes to zero, is calculated to be 0.9798 for the present model. Finally, although the modified model wave function does not satisfy the real cusp condition at the nucleus, the shape of the radial density computed for the He atom is rather good if compared with the accurate DMC one.

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Z	ξ_{opt}	λ_{opt}	$H(\xi_{opt}, \lambda_{opt})$	HF	$s-$wave	correlated
1	0.9144	0.4940	-0.50648	-0.48793	-0.51450	-0.52775
2	1.8560	0.3392	-2.87273	-2.86168	-2.87903	-2.90372
3	2.8477	0.3212	-7.24646	-7.23642	-7.25249	-7.27991
4	3.8443	0.3139	-13.62094	-13.61130	-13.62686	-13.65557
5	4.8424	0.3100	-21.99566	-21.98623	-22.00151	-22.03097
6	5.8412	0.3076	-32.37048	-32.36119	-32.37629	-32.40625
7	6.8404	0.3059	-44.74535	-44.73616	-44.75114	-44.78145
8	7.8398	0.3047	-59.12026	-59.11114	-59.12603	-59.15660
9	8.8393	0.3037	-75.49520	-75.48613	-75.50095	-75.5317(*)
10	9.8390	0.3030	-93.87014	-93.86111	-93.87588	-93.9068(*)

Table 1: Optimal parameters and minimal energies (atomic units) for He-like ions. Comparison with Hartree-Fock (HF), s-wave model and fully correlated data [9]. Fully correlated energies of F^{7+} and Ne^{8+} (*) have been obtained from correlation energies calculated by Clementi [10] summed to our HF energies.

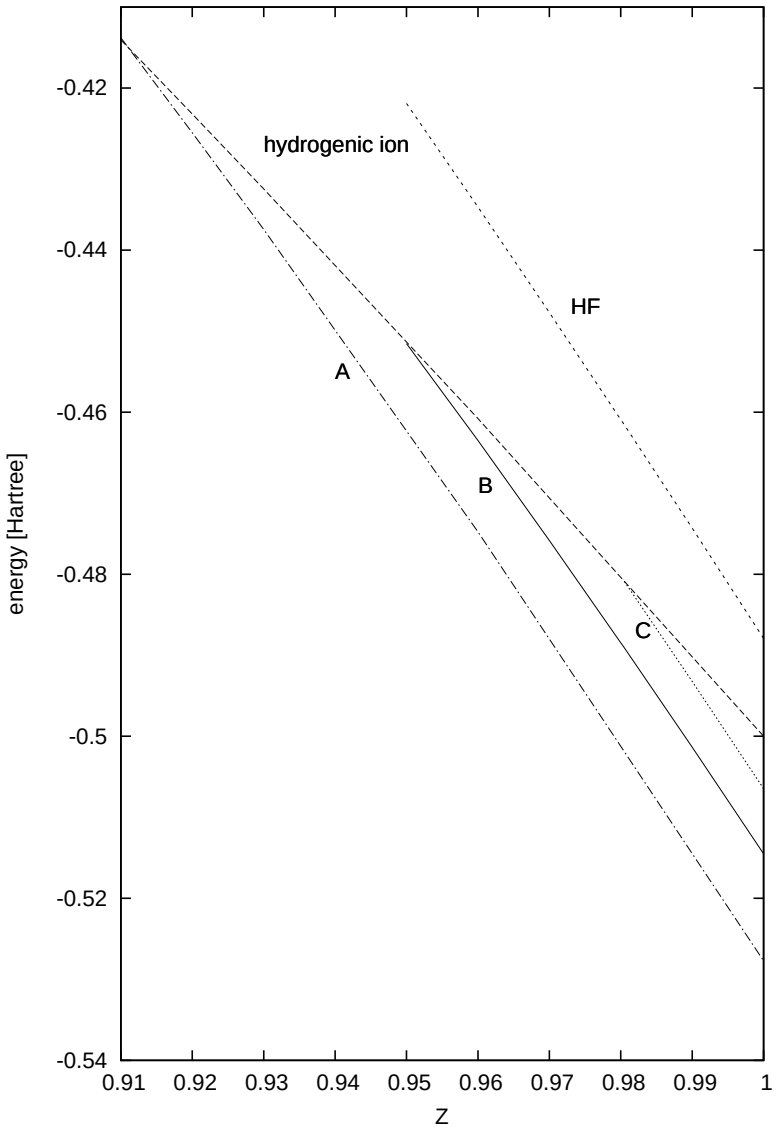

Figure 1: Energy curves of He-like ions against the nuclear charge Z compared with the energy of corresponding hydrogenic ions. Curves are for fully correlated [11] calculations (A), for the s-wave model (B), for $H(\xi_{opt}, \lambda_{opt})$ (C) and for Hartree-Fock (HF).

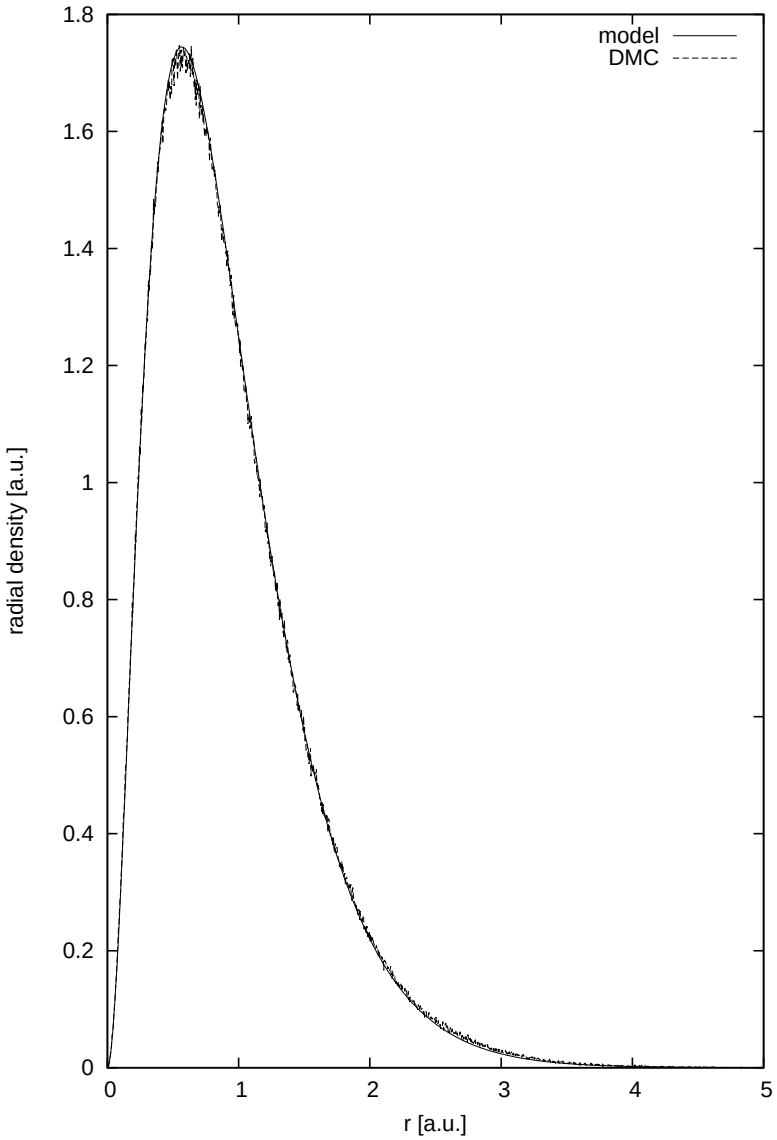

Figure 2: Comparison between DMC and model (from $\Psi[\xi_{opt}, \lambda_{opt}]$) radial density of He